

# Non-equilibrium condensation and coarsening of field-driven dipolar colloids

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**Abstract** – In colloidal suspensions, self-organization processes can be easily fueled by external fields. One particularly interesting class of phenomena occurs in monolayers of dipolar particles that are driven by rotating external fields. Here we report results from a computer simulation study of such systems focusing on the clustering behavior also observed in recent experiments. The key result of this paper is a novel interpretation of this pattern formation phenomenon: We show the clustering to be a by-product of a vapor-liquid first order phase transition. In fact, the observed dynamic coarsening process corresponds to the spindodal demixing that occurs during such a transition.

**Introduction.** – Self-assembly and self-organization processes of colloidal particles are topics that have been receiving much attention in the recent past.

Indeed, such systems display a multitude of equilibrium and non-equilibrium self-assembled structures, examples being lane formation [1, 2], shear banding [3], the coiling up of magnetic chains [4], and the wide range of patterns observed in particles immersed in liquid crystals [5]. Here, we are particularly interested in colloidal systems involving dipolar interactions. Prime examples of the resulting self-assembled structures include chain formation in constant external fields [6–8], layer formation in rotating fields [7–10], and the structure formation of colloidal particles in triaxial fields [11–13].

Up until recently, most works on self-organization under the influence of time-dependent external fields focused on *induced* dipolar particles. A noteworthy exception is a paper by Murashov and Patey, in which layer formation of rotationally driven colloidal particles carrying a permanent dipole moment was investigated [14].

A particularly interesting self-organization process occurs when colloidal particles are exposed to rotating fields in a quasi-two-dimensional geometry. In this situation, the external fields are found to induce the formation of two-dimensional clustered structures. Not only does this work for particles in which a dipole moment can be induced [15–17], but also for particles carrying a permanent dipole moment. This was recently shown by Weddemann

and coworkers in an experimental study [18, 19].

In the present paper, we want to pick up on this phenomenon and provide a novel interpretation of the two-dimensional cluster formation process. Specifically, we will show that this self-organization process is a by-product of an equilibrium liquid-vapor phase transition.

We investigate the colloidal system by making use of different computer simulation techniques. In these simulations, we use dipolar particles in a quasi-two-dimensional geometry to model the system. This means that the dipoles can rotate freely in all the spatial directions while the translational motion is restricted to a two-dimensional plane. We use Brownian dynamics simulations to understand the dynamical properties of the system and Wang-Landau-Monte-Carlo simulations to look into its phase behavior. Additionally, to assess the influence of the solvent on the system, we take it implicitly into account by employing Brownian dynamics simulations that include hydrodynamic interactions.

This paper is organized as follows: After introducing the model and the different simulation techniques, we first discuss the full non-equilibrium “phase” diagram indicating the region of cluster formation in the domain of frequency and strength of the external field at constant equilibrium thermodynamic parameters. In a next step, we investigate the influence of hydrodynamic interactions on the formation of clusters. Then we present the principal point of this paper: We show that the non-equilibrium cluster for-

mation is essentially an equilibrium phase transition. To do this, we calculate an equilibrium phase diagram, in the construction of which an effective non-time-dependent inter-particle interaction is used, and examine the growth of the characteristic domain size of the clusters. The paper is then closed with a brief summary and conclusions.

**Model.** – To model the (dipolar) colloidal particles in our simulations we use a dipolar soft sphere (DSS) potential, which is comprised of a repulsive part  $U^{\text{rep}}$  and a point dipole-dipole interaction part

$$U^{\text{DSS}}(\mathbf{r}_{ij}, \boldsymbol{\mu}_i, \boldsymbol{\mu}_j) = U^{\text{rep}}(r_{ij}) - \frac{3(\mathbf{r}_{ij} \cdot \boldsymbol{\mu}_i)(\mathbf{r}_{ij} \cdot \boldsymbol{\mu}_j)}{r_{ij}^5} + \frac{\boldsymbol{\mu}_i \cdot \boldsymbol{\mu}_j}{r_{ij}^3}. \quad (1)$$

In eq. (1),  $\mathbf{r}_{ij}$  is the vector between the positions of the particles  $i$  and  $j$ ,  $r_{ij}$  its absolute value, and  $\boldsymbol{\mu}_i$  is the dipole moment of the  $i$ th particle. The potential  $U^{\text{rep}}$  is the (shifted, cf. [20]) soft sphere (SS) potential for particles of diameter  $\sigma$ , with the unshifted SS potential being given by  $U^{\text{SS}}(r) = 4\epsilon(\sigma/r_{ij})^{12}$ .

We investigate the system by making use of different simulation techniques. First, we employ non-overdamped Brownian dynamics (BD) simulations. The corresponding equations of motion for particles of mass  $m$  and moment of inertia  $I$  are [14, 21]

$$m\ddot{\mathbf{r}}_i = \mathbf{F}_i^{\text{DSS}} - \xi_T \dot{\mathbf{r}}_i + \mathbf{F}_i^{\text{G}} \quad (2)$$

$$I\dot{\boldsymbol{\omega}}_i = \mathbf{T}_i^{\text{DSS}} + \mathbf{T}_i^{\text{ext}} - \xi_R \boldsymbol{\omega}_i + \mathbf{T}_i^{\text{G}}, \quad (3)$$

where  $\xi_T$  and  $\xi_R$  are the translational and rotational friction coefficients, respectively. Consistent with earlier simulation studies of ferrofluidic particles [10, 14],  $\xi_T = 13.5\sqrt{m\epsilon/\sigma^2}$  and  $\xi_R = 0.45\sqrt{m\epsilon\sigma^2}$  were used. Furthermore,  $\boldsymbol{\omega}_i$  is the angular velocity of particle  $i$ ,  $\mathbf{F}_i^{\text{G}}$  and  $\mathbf{T}_i^{\text{G}}$  are random Gaussian forces and torques whose variance is related to the friction coefficients [14], and  $\mathbf{T}_i^{\text{ext}}$  are torques due to an external field. The field is homogeneous, rotates in the dipolar monolayer, and is given by

$$\mathbf{B}(t) = B_0(\mathbf{e}_x \cos \omega_0 t + \mathbf{e}_y \sin \omega_0 t), \quad (4)$$

where  $\omega_0$  is the frequency of the field and  $B_0$  its strength.

The equations of motion (2) and (3) were integrated with a Leapfrog algorithm [20] using a time-step of  $\Delta t = 0.0025(m\sigma^2/\epsilon)^{1/2}$  and 4900 or 1225 particles, respectively.

Further, to investigate the influence of a solvent within our implicit model, we use a Brownian dynamics simulation that includes hydrodynamic interactions between the particles. These interactions are incorporated up to third order in the diffusion tensor for the translation-translation coupling, the rotation-rotation coupling, and the translation-rotation (and vice versa) coupling [22, 23]. The tensor describing the translation-translation coupling is the well known Rotne-Prager tensor. The other couplings incorporate the influence of the additional rotational degrees of freedom. The time evolution equations

that were used can be found in [23] and we used 324 particles in these simulations.

Finally, to investigate the equilibrium phase behavior of the system (based on a time-averaged potential, see eq. (5)), we use Monte Carlo (MC) simulations in the Grand-canonical ensemble. In general, first-order phase transitions are plagued by a large free energy barrier separating both phases, making unbiased sampling very inefficient. In order to overcome the barrier we use a method proposed by Wang and Landau [24] which significantly improves the sampling by adding a weight-function to the simulation. Details of the method applied to dipolar systems in two dimensions can be found in [25].

In the case of BD and MC simulations we deal with the long-ranged dipolar interactions by using the Ewald summation method [26]. In our hydrodynamic simulations, on the other hand, we only consider a single simulation box filled with dipolar particles.

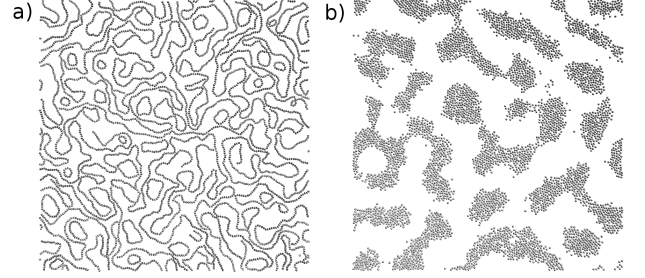


Fig. 1: Snapshots showing a system in zero field (a) and exposed to a rotating field of strength  $(\epsilon/\sigma^3)^{1/2}B_0 = 50.0$  and frequency  $(m\sigma^2/\epsilon)^{-1/2}\omega_0 = 20$  (b). Snapshot (b) was taken at time  $t = 375(m\sigma^2/\epsilon)^{1/2}$  after the start of the simulation. 4900 particles were used.

**Synchronization and cluster formation.** – A snapshot of a quasi-two-dimensional system ( $\rho\sigma^2 = 0.3$ ,  $k_B T/\epsilon = 1.0$ ) of strongly coupled dipolar particles ( $\lambda_{\text{DD}} = \mu^2/k_B T \sigma^3 = 9$ ) at zero field is shown in fig. 1a. As is typical for such dipolar systems the particles align in a head-to-tail configuration, which, in a two-dimensional geometry, results in the formation of chains and rings [27].

If we expose such a system to a rotating in-plane field of sufficient strength and frequency, we observe the particles agglomerate into two dimensional clusters. An example of this can be seen in fig. 1b. The observed clustering behavior already indicates that there are attractive interactions in the system, which play a crucial role. The origin of these interactions can be rationalized as follows: Averaging the dipolar inter-particle interaction potential over one rotational period of the field under the assumptions that the particles do not move translationally and rotate synchronously with the field (i.e. follow the field at constant phase difference) yields

$$U^{\text{ID}}(\mathbf{r}_{ij}) = -\frac{\mu^2}{2r_{ij}^3}. \quad (5)$$

Clearly, for (5) to be a good approximation to the true inter-particle interaction, it is crucial that essentially all the particles follow the field. An extensive analysis of this synchronization behavior of the dipolar particles with the field in three dimensions can be found in [10, 28].

To systematically investigate the appearance of synchronization and clustering we scanned a wide range of frequencies and field strengths. We consider a system as clustered if the particles have on average more than 2.3 neighbors within a distance of  $1.7\sigma$  from their center. The latter value was used, since it is slightly larger than the typical distance between neighboring particles in a clustered system. This was found by looking at the first minimum of respective pair correlation functions. The fact that we require 2.3 neighbors on average ensures that two-dimensional aggregates are counted as clusters while chainlike structures are disregarded.

The results of this investigation of the space of the field parameters can be seen in fig. 2. Depicted are three distinct regions, denoted “synchronous”, “synchronous/clustered”, and “not synchronous”. The first region is comprised of systems in which the particles rotate synchronously with the field but do not form clusters. Within this region, chains in the direction of the field can be observed at low frequencies while spatial inhomogeneities begin to appear at larger frequencies. As also becomes apparent here, a minimal  $B_0$  is required for the field to align the particles with itself.

In the second region, the synchronous rotation continues but is now accompanied by the formation of two-dimensional clusters. This indicates that the effective inter-particle potential becomes sufficiently isotropic within this region to be reasonably described by the averaged dipolar potential (5).

As expected, the diagram in fig. 2 also depends on the friction coefficients used in the BD simulations. In particular, we found the size of the synchronous regime in the frequency domain to shrink in favor of the “clustered” regime if the translational friction coefficient  $\xi_T$  is increased. This results from reduced displacement of the particles after one rotational period of the field thereby making eq. (5) valid at much lower driving frequencies.

In the third region, we find neither synchronization nor cluster formation. Clearly, the lack of synchronization is the direct cause of the breakdown of cluster formation (cf. eq. (5)). The loss of synchronization occurs, since the torques on the particles due to the external field become unable to overcome the torques due to the rotational friction (similarly to what is seen in three dimensions [10]).

Given the clustering scenario and our explanations so far, it is important to ask to which extent the BD simulations can describe the dynamics of the real colloidal system. The latter includes, by definition, a solvent. The rotating external field, which constantly generates rotational motion of the particles, will create flow fields that can result in considerable motion of the particles. This

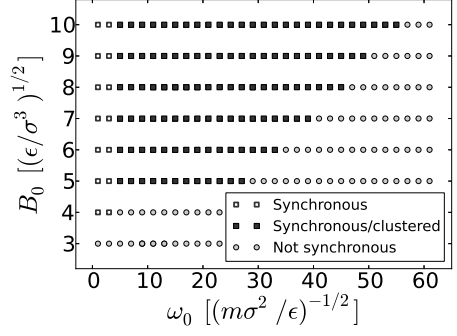


Fig. 2: Synchronization behavior and cluster formation depending on frequency  $\omega_0$  and strength  $B_0$  of the field. The density and temperature of the system used were  $\rho\sigma^2 = 0.2$  and  $k_B T/\epsilon = 1.0$ , respectively. 1225 particles were used in these simulations.

might influence the cluster formation phenomenon due to the following reason: The averaged potential (5) is only valid as an approximation to the true inter-particle interaction if the translational motion of the particles during one rotational period of the field is small.

Hence, in order to find out whether cluster formation persists when hydrodynamic interactions are present, we built a simulation that takes these into account. To assess their influence on the cluster formation, it is sufficient to consider only a single simulation box filled with particles.

We considered a number of state points ( $\rho\sigma^2 = 0.1, 0.2, 0.3$ ,  $k_B T/\epsilon = 1.0, 1.8$  at  $\omega\sigma^2/D_0 = 250$ ,  $B_0(\sigma^3/\epsilon)^{1/2} = 80$ ) in our simulations with and without hydrodynamic interactions included. We found that cluster formation occurs in both these cases at all the considered densities and temperatures, with a single cluster eventually forming in the simulation box. This can be seen in fig. 3, where we show snapshots of the evolution of a rotationally driven system. The snapshots in the top row show a system in which hydrodynamic interactions are not taken into account, while hydrodynamic interactions are present in the snapshots in the lower row. Another important point that is illustrated by fig. 3 is that the cluster formation process is considerably accelerated by the hydrodynamic interactions. At the intermediate time ( $t' = 10.8$ ), only a single cluster remains in the hydrodynamically interacting system (fig. 3e), while it takes much longer for the not hydrodynamically interacting system to reach the same state (cf. fig. 3b,c).

Accelerated cluster formation is a direct consequence of both the translation-translation and rotation-translation coupling. In particular the former coupling accelerates the formation of clusters. This can be inferred from selectively switching off the different hydrodynamic couplings. Further, note that if hydrodynamic interactions are present, the cluster rotates rapidly around its center, which is not the case if these interactions are absent. Here, the sole cause is the hydrodynamic rotation-translation coupling.

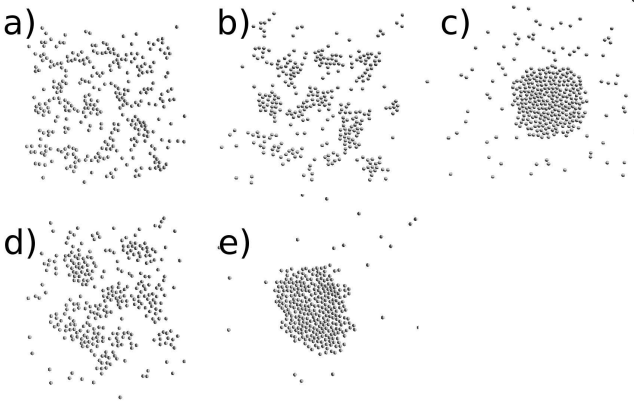


Fig. 3: Snapshots of a system at different times without (top) and with (bottom) hydrodynamic interactions. The snapshots in the first column were taken at  $t' = 2.5$ , the ones in the second column at  $t' = 10.8$ , and the one in the last column at  $t' = 138.5$  after the start of the simulation. Note that  $t' = tD_0/\sigma^2$ .

Thus, the hydrodynamic interactions affect the (rotational) cluster motion but do not hinder the particles in the cluster formation process at all.

**Relation to condensation.** – Given the clustering behavior of the non-equilibrium, yet fully synchronized, field-driven system, we now ask to which extent the behavior of the system can be understood by that of an *equilibrium* system interacting via the effective interaction given by eq. (5) (as well as the repulsive potential  $U^{\text{rep}}$  (cf. eq. (1))). More precisely, our hypothesis is that the observed cluster formation stems from an equilibrium, first-order phase transition between a vapor and a liquid phase. To test this hypothesis, we have performed Wang-Landau-Monte-Carlo simulations of a system interacting via  $U^{\text{ID}}$  (eq. (5)) [30].

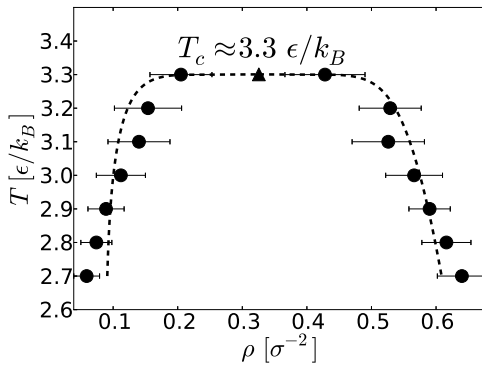


Fig. 4: Phase diagram in the  $T$ - $\rho$  domain at  $(\epsilon\sigma^3)^{1/2}\mu = 3$ .  $T_c$  denotes the critical temperature, the solid line corresponds to the binodal representing coexisting gas and liquid states.

The key result we obtained from these simulations is the phase diagram presented in fig. 4. The presence of a binodal shows that there is indeed a gas-liquid phase

transition in the non-driven system.

Moreover, if we now compare this phase diagram with the thermodynamic state point related to our non-equilibrium system (see e.g. fig. 1b), we find that the latter ( $\rho\sigma^2 = 0.3$ ,  $k_B T/\epsilon = 1$ ) lies well within the two-phase region. This finding clearly suggests that the cluster formation observed in the (fully synchronized) field-driven system is spinodal decomposition, i.e., a dynamic phenomenon occurring during a first-order phase transition. To check this conjecture in more detail, we looked at the time evolution of the cluster sizes  $\ell$ . For phase separating systems it is well established that  $\ell$  exhibits power law behavior [31], i.e.  $\ell \propto t^\alpha$ , with the corresponding exponents depending on the growth stage. Such a behavior is also seen in Molecular dynamics (MD) simulations. In particular, domains with growth proportional to  $t^{1/2}$  [32, 33] and  $t$  [34] have been identified.

These power laws are universal in MD simulations but they do not necessarily apply to BD simulations with their modified equations of motion. This was shown, e.g., by Lodge and Heyes for the case of overdamped BD [35]. At the same time, however, the clusters in ref. [35] were still found to grow with a power law. To check for the existence of cluster growth with a power law in non-overdamped BD simulations, we first investigated a “reference system”, whose equilibrium behavior is well studied. Specifically, we considered a two-dimensional Lennard-Jones system at  $\sigma^2 = 0.3$ ,  $k_B T/\epsilon = 0.45$  with the critical point being at  $\rho\sigma^2 \approx 0.335$ ,  $k_B T/\epsilon \approx 0.533$  [36]. Investigating the domain size, we did indeed find a power law dependence  $\ell \propto t^\alpha$  with  $\alpha \approx 0.30$ . Note that the cluster size was obtained by measuring the distance at which the pair correlation function assumes a value of one for the first time if the radial bins are taken to be larger than the particle diameters (cf. [37]).

Similarly, we checked the cluster growth for a driven dipolar system and a system interacting via the potential  $U^{\text{ID}}$ . In the simulations we used a density and a temperature of  $\rho\sigma^2 = 0.3$  and  $k_B T/\epsilon = 1.5$ , respectively, which put the systems well inside the coexistence region of fig. 4. The domain sizes over time that were extracted from the simulations are shown in fig. 5. As can be seen, the cluster sizes of these two systems are almost identical at any given time. In particular, the characteristic domain sizes grow with a power law  $\ell \propto t^\alpha$  with  $\alpha$  being equal to 0.36 in both cases. We note that this is almost identical to the Lifshitz-Slyozov growth law ( $\ell \propto t^{1/3}$ ) [31].

From these two results we conclude that the non-equilibrium system does indeed undergo spinodal decomposition. First, the cluster growth proceeds with a power law, which is typical within the spinodal region. Second, the growth behavior remains unchanged even if the interactions between the driven dipoles are replaced with the effective ones. This emphasizes the similarity between those two systems and once more shows the validity of the phase diagram for the driven system.

Note that hydrodynamic results are not included in



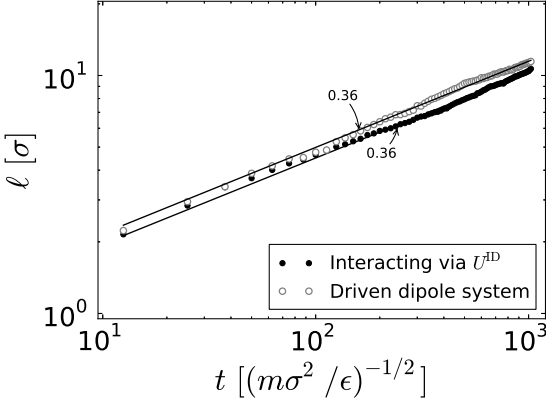


Fig. 5: Cluster growths for a system interacting via the effective potential and a system that is driven by an external rotating field at density  $\rho\sigma^2 = 0.3$  and temperature  $k_B T/\epsilon = 1.5$  (state inside the coexistence region of fig. 4). 4900 particles were used in the simulations.

fig. 5. We only considered 324 particles in these simulations and additionally did not use periodic boundary conditions. This makes an accurate determination of the cluster growth very difficult.

**Conclusions.** – In this paper we have investigated the formation of two-dimensional aggregates in monolayers of dipolar particles that are driven by rotating external in-plane fields.

The first result of this paper is a non-equilibrium “phase” diagram, which shows the regions of synchronization and cluster formation in the  $\omega - B_0$ -domain. At high frequencies the synchronization of the particles with the field breaks down, which results in a breakdown of cluster formation. Similarly, we do not find cluster formation at low frequencies. Here, the effective interaction between the particles is not well enough described by  $U^{ID}$ , since the particles move considerably during one rotational period of the field. This changes in-between those frequencies, where the particles rotate synchronously and sufficiently fast, which leads to the formation of clusters.

Next, we investigated the stability of the clustering phenomenon when hydrodynamic interactions are present. In our simulations, we found the phenomenon to persist despite these interactions. In fact, the cluster formation seems to proceed at even faster rates with these interactions included. We attribute this to a combination of the hydrodynamic translation-translation and rotation-translation coupling. The former seems to accelerate the formation of clusters while the latter leads to the quick formation of a single cluster in the center of the simulation box.

Test simulations indicate that these interactions have additional consequences: Compared to a non-hydrodynamically interacting system, they seem to allow for the formation of clusters at lower driving frequencies

and therefore affect the non-equilibrium “phase” diagram in fig. 2. To study the precise influence of the hydrodynamic interactions is outside of the scope of this paper, but would be very illuminating in its own right.

We concluded our analysis with the main result of this letter: We established the clustering phenomenon to be a by-product of a liquid-vapor phase transition. This was done in two steps: We began by uncovering a phase transition via Wang-Landau-MC simulations in a system interacting via the effective potential  $U^{ID}$ . Recall that this potential describes the interactions between the particles very well in the driven system at sufficiently high frequencies. In a next step we examined the domain growth of the driven system within the binodal region of the phase diagram. As expected within the spinodal region of a liquid-vapor phase transition, we found the characteristic cluster size to grow with a power law. Additionally, it essentially agrees with the domain growth of the non-driven system interacting via the effective potential  $U^{ID}$ . These facts lead us to conclude that the clustering process corresponds to the pattern formation occurring inside the binodal of a vapor-liquid phase transition.

Given these findings, it is interesting to compare them to recent experimental results. Indeed, cluster formation in monolayers resulting from a rotating external field has been observed multiple times [15–19]. In most of these publications induced dipolar particles are brought to self-assemble into two-dimensional aggregates. The only paper in which particles with a permanent dipole moment were used (ref. [18]) features a dipole-dipole coupling strength ( $\lambda_{DD} = \mu^2/k_B T \sigma^3$ ) that is dominated by the dipole-field coupling strength ( $\lambda_{DF} = \mu B_0/k_B T$ ). There, the ratio  $\lambda_{DF}/\lambda_{DD}$  is about 6, which is larger than the largest ratio that appears in fig. 2. Consequently, we expect the particles in [18] to rotate synchronously with the field, resulting in the effective interaction  $U^{ID}$  and the observed cluster formation.

The clusters found in the literature are typically hexagonally ordered. In our simulations this becomes more and more true with increasing frequency and strength of the field as well as with decreasing temperature. It should be noted, however, that our BD simulations involve large Brownian kicks, which result in deviations from the hexagonal structure. In the references [15, 17–19], micrometer-sized particles were used, which makes these contributions much less significant leading to more pronounced order.

Further, the driving frequencies used in these publications are considerably smaller than the ones used here. This can once again be explained by the size of the particles: Larger particles typically have smaller friction coefficients, which, as test simulations show, result in cluster formation at lower frequencies of the field.

The coarsening process investigated in this paper can universally be observed in phase separating systems. Condensation transitions and spinodal demixing in binary fluids or metallic alloys are popular examples of this. The process reported in this letter is exceptional, however, in

that the existence of a liquid-vapour transition in ordinary dipolar system is still a hotly debated topic and one of the big unresolved questions regarding these particles [38,39]. But as shown here, such a phase transition can be induced via an external driving field.

The system considered in this study is driven and, consequently, inherently in a non-equilibrium state. The dynamic coarsening observed in spinodal decomposition, on the other hand, is a process typically associated with non-driven systems. It is, however, not unique to those. For instance, active Brownian swimmers performing a “run-and-tumble” motion such as *E. Coli* bacteria, exhibit similar clustering behavior and demixing [40]. With the ongoing and rising interest in dynamics and non-equilibrium processes we expect an increasing amount of systems to be uncovered that are driven into cluster or pattern formation with behaviors similar to the one described here.

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